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Bonding of an Isolated K atom to a Surface: Experiment and Theory

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We present a new and general technique with which the local properties of the unoccupied states of an adsorbed alkali atom in the low coverage limit can be studied. The method, based on a combination of experimental core level spectroscopy data and calculations, is demonstrated for the K/graphite system. We show that core excitation and decay spectra of adsorbed Ar combined with the calculations form a most powerful tool in order to determine the unoccupied density of states for an isolated K adatom. We find that the $4s$ level of an isolated K atom on graphite is placed 2.7 eV above E_F , with a hybridization width of the order of only 0.1 eV. [S0031-9007(97)03461-3]

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The adsorption of alkali metals on solid surfaces has long served as a prototype for simple chemisorption [1]. However, there is an ongoing debate concerning the most fundamental aspects of the adsorption bond. This is especially the case for the *low coverage limit*, which corresponds to the theoretically ideal situation where only the alkali-substrate interaction has to be considered [2–8]. A particularly controversial issue concerns the nature of the alkali ns -derived level, which is the key for an understanding of the adsorption bond. This is connected to the well-known simple criteria for ionic vs covalent bonding: In an ionic bond, the ns resonance is narrow and empty and thus is situated above the Fermi level (E_F), whereas in a pure covalent bond, the ns resonance straddles E_F and is essentially half-filled [2,3]. An interesting system which shows a well-characterized transition between these two cases as a function of coverage is K/graphite. At coverages below 0.1 ML, a dispersed phase is found in which the adatoms are spread uniformly on the surface [8–10]. This phase has been suggested to be significantly ionic [9,11,12], in line with experimental evidence [8] for significant charge transfer into the substrate. At higher coverages (0.1–1.0 ML), a metallic (2×2) phase is formed [8].

In this Letter, we present a new method with which unique and vital information about the K-graphite bonding is obtained. We employ core-level spectroscopies combined with first principles theory in order to unambiguously identify the K-derived $4s$ level and discuss its properties. Using the fact that the final state of a core-excited Ar atom is similar to K (the $Z + 1$ approximation), we show that core excitation and decay spectra for adsorbed Ar and calculations provide consistent results for the *location* and *bonding-induced width* of the $4s$ resonance for an adsorbed K-atom at the adsorbate-substrate distance for Ar. By adjusting in the theory for the differences in distance above the surface between adsorbed Ar and K, the unoccupied density of states (DOS) for an iso-

lated K atom on graphite is determined for the first time. Finally, we indicate how the method can be generalized to other alkali adsorption systems.

The experiments were performed at MAX-lab. The experimental setup is discussed in detail elsewhere [13]. The photon energy resolution was 0.15 eV and the electron energy resolution 0.3 eV. Photon energies were calibrated by measuring a given spectral feature using both first and second order light at the same monochromator setting, such that the difference is the photon energy. X-ray absorption (XA) spectra were taken in partial Auger yield mode. The sample, highly oriented pyrolytic graphite (HOPG), was cooled to less than 25 K. The Ar monolayer was prepared by formation of multilayers followed by desorption until only one Ar $2p_{3/2}$ component was observed in the photoemission spectrum.

The theoretical calculations were based on a full potential linear muffin tin orbital method in a slab geometry [14] and were performed for a single graphite layer with a K atom on the surface. In order to simulate dispersed K chemisorbed on graphite, we used a large supercell of 18 C atoms and one K atom to minimize the K-K interaction. To remove residual K-K bonding effects, we explicitly switched off the interaction between K atoms by writing the matrix elements of the K $4s$ states of the Hamiltonian as $\langle 4s|H|4s \rangle = \epsilon_{4s} \langle 4s|4s \rangle$, i.e., as the atomic $4s$ level times the overlap matrix element. The $4p$ orbitals of K were treated in the same way. The atomic levels ϵ_{4s} and ϵ_{4p} were taken from an atomic calculation in the presence of the graphite potential. In the displayed DOS spectrum the Fermi level was placed at the same position as for the pure graphite layer, since the displacement due to adsorption of an isolated K atom is negligible. In order to reduce the computational efforts we only considered a single graphite layer, an approximation tested previously [15]. Moreover, the irreducible part, $\frac{1}{6}$, of the two-dimensional Brillouin zone was sampled at 10 \mathbf{k} points. In the last iteration 36 \mathbf{k} points were used to more accurately determine the DOS.

The photoelectron binding energy (BE) of the Ar $2p_{3/2}$ peak obtained by x-ray photoemission spectroscopy (XPS) and the photon energy (PE) needed for the $2p_{3/2} \rightarrow 4s$ excitation as measured by x-ray absorption spectroscopy (XAS) give the energy relationship between a core ionized ($2p_{3/2}^{-1}$) and a neutral core-excited ($2p_{3/2}^{-1}4s^1$) species on the surface. Figure 1 shows the Ar $2p_{3/2} \rightarrow 4s$ XAS spectrum for 1 ML Ar on graphite on a relative energy scale, where zero represents the corresponding $2p_{3/2}$ BE relative to the graphite Fermi level. It is found that the first XAS peak, i.e., the $4s$ resonance, has a positive energy on this scale, meaning that the XPS final state has a lower energy. Since the XPS final state corresponds to an ionic species on the surface and a screening charge in the substrate, it can be concluded that an ionic configuration is energetically favorable [16]. Moreover, when we discuss the empty valence electron states of the system, the zero point on this energy scale can be envisaged as the Fermi level of the system [16,17]. This implies in turn that for 1 ML Ar on graphite, there is an empty $4s$ resonance well above E_F .

The DOS observed in XAS corresponds to that of the core-excited final state [17]. Hence, to the extent that the $Z + 1$ approximation is accurate, the XAS spectrum of adsorbed Ar provides the location of the local unoccupied states of adsorbed K. From Fig. 1, one may therefore infer that the $4s$ resonance for a K-like Ar atom embedded in an Ar monolayer is situated 2.1 eV above the Fermi level. To determine the $4s$ resonance position of an isolated K-like Ar atom, effects caused by the surrounding Ar atoms have to be considered: The $4s$ resonance will be shifted upwards approximately 0.25 eV due to the additional spatial confinement of the $4s$ orbital [18]. Polarization screening in the dense 2D Ar layer will shift the Ar $2p$ ionization potential downwards with a similar amount [19]. Thus, the $4s$ resonance for an isolated, K-like Ar atom will be situated 1.6 eV above E_F .

The results of the first principles calculations are shown in Fig. 2. These were performed for a K atom positioned

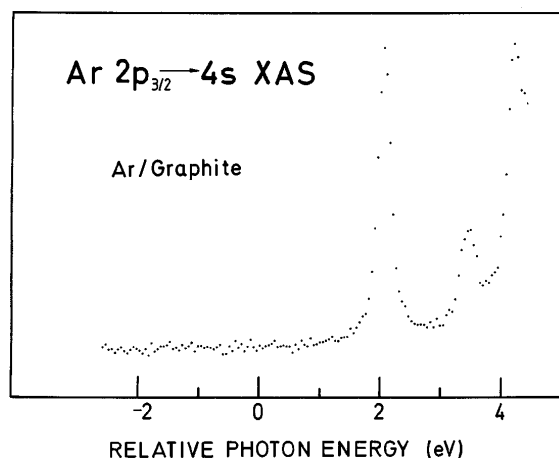


FIG. 1. Ar $2p_{3/2} \rightarrow 4s$ XAS spectra for 1 ML Ar on graphite. The zero point is equivalent to E_F for the system, given by the Ar $2p_{3/2}$ BE (see text).

at 2.6 and 3.2 Å above the graphite layer, corresponding to the experimentally observed bond distances of K and Ar on graphite [12,20]. The K atom is assumed to be located at a hollow site. Calculations of core-excited Ar and ground state K give almost indistinguishable values of the $4s$ peak position and width, demonstrating the accuracy of the $Z + 1$ approximation. As is clear from Fig. 2, the results for the Ar-graphite bond distance reproduce the experiment very well: The theoretical value of the $4s$ position is $E_F + 1.7$ eV, only 0.1 eV above the experimental value.

Further information can be gained from the core hole decay spectra. The XPS and XAS final states have finite lifetimes, after which they decay primarily through electron emission; the decay of the core-ionized state (XPS) is denoted Auger decay, whereas the decay of the core-excited state (XAS) is denoted autoionization decay. In gas phase these decay channels are very different [21], which, however, may not be the case for an adsorbed species, since there may be charge exchange between the adsorbate and the substrate prior to the electron emission.

For chemisorbates, where rapid charge-transfer screening of the core-ionized state occurs, the difference between Auger and autoionization spectra is minimal [22,23]. For physisorbates, where the XPS final state is not charge-transfer screened, the decay spectra are generally found to be gas-phase-like. However, charge exchange between the adsorbate and the substrate may occur, but at a much lower

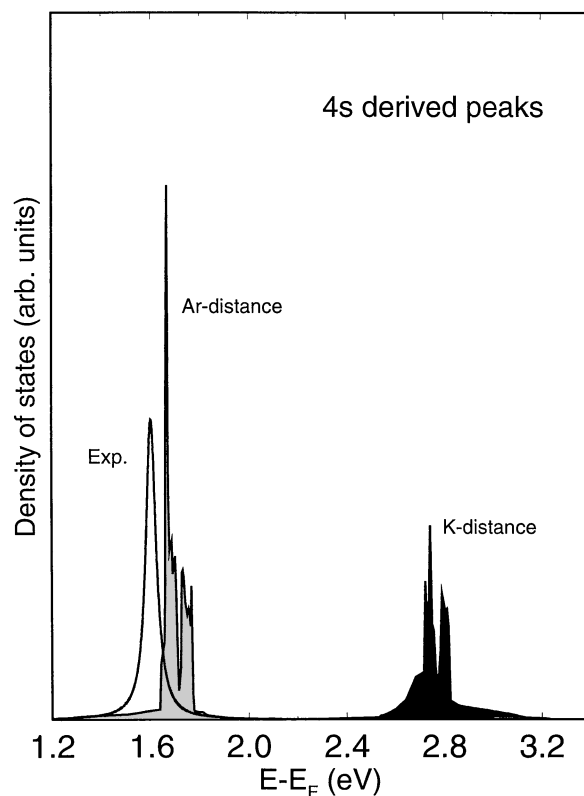


FIG. 2. Calculated DOS for K adsorbed on graphite for two bond distances, with E_F at 0.0. The experimental results are represented by a Lorentzian with FWHM 0.05 eV (see text).

rate, as first observed for N_2 /graphite [24]. In this case, the Auger spectrum was found to consist of two sets of features; those originating in decay from ionic and neutral core hole states, respectively. Since the energy of the core-ionized state is larger than the energy of the lowest neutral core-excited state, this implies that charge transfer from substrate to adsorbate occurs on the time scale of the core hole decay in order to reach the lowest-energy core hole configuration. In a simple model, in which the charge-transfer rate (τ_{CT}) and the Auger rate governed by the core hole lifetime (τ_I) is exponential, it can be shown that the probability for decay from the neutralized state, given by the intensity ratio between the two processes in the core hole decay spectrum, equals $(1 + \tau_{CT}/\tau_I)^{-1}$ [24]. Thus, with knowledge of the core hole lifetime, a characteristic charge-transfer time (τ_{CT}) can be derived which in turn corresponds to an interaction width, Δ_{CT} . Δ_{CT} can be viewed as a measure of the adsorbate-substrate hybridization width in the core-excited state [24].

Adsorbed Ar also shows charge-transfer processes in the core hole decay spectra [25,26]. However, the core-ionized state is lower in energy than the core-excited state for Ar/graphite (Fig. 1). Hence the neutral $2p_{3/2}^{-1}4s^1$ state generated in the XA process may decay to the $2p_{3/2}^{-1}$ ionic state via charge transfer to the substrate during the lifetime of the core hole. The autoionization spectrum recorded after $2p_{3/2} \rightarrow 4s$ excitation is shown in the upper part of Fig. 3. Charge transfer to the substrate occurs for Ar/graphite, which gives rise to Auger-like features (decay of $2p_{3/2}^{-1}$ ionic states) as seen from the comparison with the corresponding $2p_{3/2}$ Auger spectrum (solid line). The presence of Auger-like features is even clearer when one compares with the autoionization spectrum obtained for Ar coadsorbed with small amounts of K (lower part of Fig. 3): This system shows no charge transfer and the spectrum is identical to the gas phase case [21]. Using a value $\tau_I = 5.5 \times 10^{-15}$ s [27], we find for Ar/graphite that the $4s$ electron is transferred to the substrate with a characteristic charge-transfer time $\tau_{CT} = 1.3 \times 10^{-14}$ s, corresponding to a hybridization width $\Delta_{CT} = 0.05$ eV.

Thus, for an isolated K adatom at Ar distance, the autoionization results show that the $4s$ electron is transferred to the substrate, and the width of the $4s$ level due to hybridization with the substrate is of the order of 0.05 eV. It should be noted that this effect contributes to the total width observed in the XA spectrum, but is much too small compared to the lifetime broadening and photon energy resolution to be directly observed; i.e., this information can only be derived from core hole decay spectroscopy. Upon comparison with the theoretical calculations for K at Ar distance (Fig. 2), we again find very good agreement: the widths of the individual features are of the order of 0.05–0.1 eV. We can therefore conclude that the experimental data together with the calculations convincingly establish two crucial quantities of the $4s$ level: the position and the hybridization width.

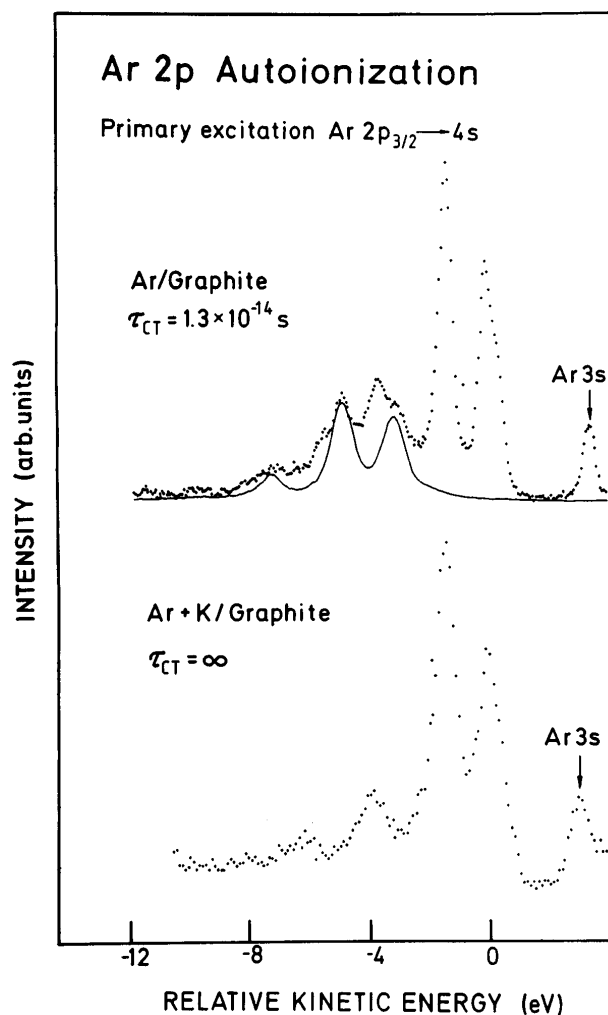


FIG. 3. Ar $2p_{3/2}$ autoionization (dotted) and Auger spectra (line). The energy scales are arbitrarily shifted to facilitate intensity comparisons. Features due to decay from $2p_{1/2}$ excited states have been subtracted from the Auger part. The charge-transfer rate (τ_{CT} , see text) has an estimated relative error of (10–15)%.

Having established the accuracy of the calculated position and width, we may estimate the effects induced by changing to K distance. As seen in Fig. 2, a decreased K-graphite distance induces an upward shift of the $4s$ level of 1.0 eV and slightly increased widths of the features. Thus, the best theoretical description of the $4s$ level for K/graphite in the dilute limit places it at $E_F + 2.7$ eV with a K-graphite hybridization width of about 0.1 eV.

Our calculations furthermore show that the graphite bands do not differ significantly from those of clean graphite, giving support for only a very small degree of covalency in the K-graphite bonding. Nevertheless, it is reasonable to assume that the substantial shift of the $4s$ level when changing from Ar-graphite distance to K-graphite distance is due to the covalent contribution to the bonding [28].

Returning to the fundamental question of ionicity vs covalency for an isolated K adatom, the facts that the

4s peak is situated above E_F and is very narrow suggest that the bonding of dispersed K on graphite is ionic. This conclusion is further corroborated by the theoretically observed charge transfer from the region around the K atom to the graphite plane. It is, however, not meaningful to give a precise number of the charge transfer since it is not a well-defined quantity [29,30].

The present approach opens the possibility to quantitative studies of a number of related systems. Experimentally, monolayers of all noble gases, except He, can be prepared on any surface. Studies of these systems can provide experimental input for adsorbed Na-Fr on the same surface. The theoretical treatment requires information about the adsorption distances for the noble gas and the $Z + 1$ alkali atom, and it becomes important to determine the sensitivity of the calculations to uncertainties in this distance. For K/graphite, we find that changing the distance by 0.1 Å (starting from 3.2 Å) gives a shift of the 4s level as small as 0.03 eV. A related question is the exact adsorption geometry; most noble gas overlayers form incommensurate structures [31], i.e., there are no well-defined sites. Consequently, the measurements will correspond to an average behavior. Calculations with the K atom placed in the so-called on-top position show that the 4s-level peak shifts less than 0.01 eV compared to the results for the hollow site. Thus, the most important parameter is the distance, and from above a value correct within 0.1 Å appears to be sufficient. This precision is definitely possible to obtain using surface extended x-ray absorption fine structure and/or diffraction techniques and can also be reached by means of total energy calculations. The first principles calculations have no principal limitations as regards the applicability to different systems. Hence our way of combining experiment and theory has a very high potential for solving many of the controversial issues concerning alkali-adsorption systems. One particularly interesting example would be to investigate the well-known model presented by Gurney and later refined by Lang-Williams for alkali adsorption on metallic substrates [2,3].

To summarize, we have demonstrated that core-level spectroscopy of adsorbed Ar combined with electronic structure calculations provide a powerful technique for studies of the local nature of the K 4s-substrate bonding in the low coverage limit. The experimental approach is based on the similarity in the valence electron distribution between Ar with a core hole and K. This makes it possible to use theory to evaluate the bonding properties relevant for "quasi-potassium" (Ar with a core hole). The same type of calculations are then repeated, but for the adsorption distance appropriate for K. Thereby one accounts for the important energy shift due to the difference in the adsorption distances for Ar and K. This approach was employed for K/graphite. The K 4s level was found to be situated 2.7 eV above the Fermi level with an approximate K-graphite hybridization width of 0.1 eV. The bonding was found to be predominantly ionic. It is clear that the

present method has a very high potential in studies of other alkali-adsorption systems.

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